

Nafion[®]/Clay Nanocomposite Membrane for Reducing Methanol Crossover in DMFC

Young-Teak Kim, Seung-Bea Park, Min-Kyu Song, and Hee-Woo Rhee

Department of Chemical Engineering,
Sogang University, Seoul 121-742, South Korea

Introduction

Direct methanol fuel cells (DMFC) based on solid polymer electrolytes are of practical interest because of their high efficiency, very low emissions, and fast and convenient refueling [1]. There are, however, two major drawbacks to large-scale commercial use, namely, limited anode catalyst activity and methanol crossover [2]. Methanol is much more difficult to oxidize compared with pure hydrogen. Furthermore, methanol crossover through electrolyte membrane may cause a mixed potential and drastically reduces cell performance. The activity of anode catalyst can be promoted by use of suitable bimetal catalyst like Pt-Ru but perfluorosulfonic acid polymer (PFSA) membranes, represented by Nafion[®], exclusively used in DMFC application are not sufficient to be a barrier for methanol permeation. Nafion[®] membrane should be thick enough to reduce methanol crossover but thicker membrane causes lower membrane conductance and most DMFC systems show relatively lower power density than hydrogen fuel cells. Therefore, it is highly desirable to find an ionomer membrane which is able to reduce the methanol permeation significantly.

Choi *et al.* reported plasma-modification of the membrane surface and palladium-sputtering [3]. Plasma polymerized barrier and metallic blocking layers decrease pore diameter and increase the methanol permeation length, but its sluggish process may increase the overall material cost. Jung *et al.* proposed Nafion/silicon oxide hybrid membrane via in-situ sol-gel reaction of tetraethylorthosilicate (TEOS) [4]. The highest current density of 650 mA/cm² at 0.5 V was achieved only high temperature (125 °C) at the DMFC condition.

In this study, we prepared Nafion/clay nanocomposite membrane to reduce methanol permeability at low temperature range while maintaining proton conductivity of Nafion. It is known that the clay composed of stacked sheets manifestly provides high molecular barrier properties, an increase in mechanical strength as well as thermal stability when the gallery of clay was exfoliated in matrix polymer. Considering the difficulties of intercalating polymers into clays with a small interlayer distance, many research efforts have been made to organically modify the clays by inserting long chain surfactants in to the galleries of the native clay. This paper presents the characterization of a nanocomposite of Nafion with organically modified commercial montmorillonite (MMT) clay and their use for DMFC.

Experimental

Nafion gels were precipitated from commercial 5 wt% Nafion[®]/H₂O/propranol solution (Solution Technology, E.W.=1100) by evaporating alcoholic solvents at room temperature under vacuum. After they were dissolved in *N,N'*-dimethylacetamide (DMA, Aldrich) at 80 °C, Nafion/DMA solution was ultrasonically mixed with an organo-clay, (cloisite[®] 10A). Then, Nafion/clay membranes were cast on a glass substrate above 100 °C in a drying oven. The recast membranes were boiled in 1 M

hydrogen peroxide and rinsed with deionised water. Finally, the composite film was boiled in 1 M sulfuric acid followed by rinsing with deionised water several times in order to remove the excess of acid.

X-ray diffraction study were carried out with a Rigaku Rad-C 4037A1 diffractometer in symmetrical reflection geometry using CuK α emission ($\lambda=1.5406$ Å). Transmission electron microscopy (TEM) was obtained with JEM-100CX2 TEM using an acceleration voltage of 100 KV. Tensile properties of composite films were measured using an Instron 4201 tester, in accordance with ASTM D638. Test specimens were 6 mm in width and approximately 100 μ m in thickness. The grip distance was 40 mm and the crosshead speed was 25 mm/min. The proton conductivity measurements (Zahner IM6 impedance analyzer) were conducted by a coaxial probe [5]. Samples were stored in distilled water for adsorbing waters, and then wiped quickly and insert into a cell that allowed the coaxial probe to be pressed against one side of the membrane. Water content of the membrane is assumed to remain saturated during measurement over the frequency range 100 kHz to 10 MHz. The methanol permeability of membranes was measured by using different reflective index (RI) of methanol and distilled water [6]. Sample membranes were exposed to distilled water and 10 wt% methanol, respectively and R.I. detector meter detected the amount of methanol molecules passed through sample membrane.

References

1. L. Carrette, K. A. Friedrich and U. Stimming, *Fuel Cells*, **1**(1), 5 (2001).
2. A. Heinzl and V. M. Barragan, *J. Power Sources*, **84**, 70 (1999).
3. W. C. Choi, J. D. Kim and S. I. Woo, *J. Power Sources*, **96**, 411 (2001).
4. D. H. Jung, S.Y. Cho, D. H. Peck, D. R. Shin and J. S. Kim, *J. Power Sources*, **106**, 173 (2002).
5. C. L. Garner and A. V. Anantaraman, *J. Electroanal. Chem.*, **395**, 67 (1995).
6. S. R. Yoon, G. H. Hwang, W. I. Cho, I. H. Oh, S. A. Hong and H. Y. Ha, *J. Power Sources*, **106**, 215 (2002).

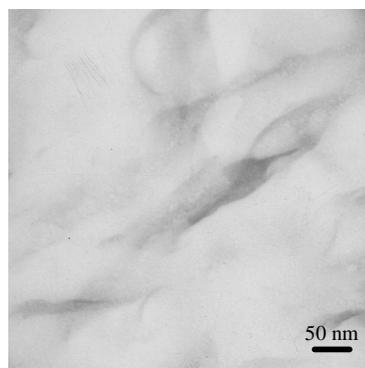


Fig. 1. TEMicrographs of 3wt% Nafion[®]/clay Nano-composite Membrane.